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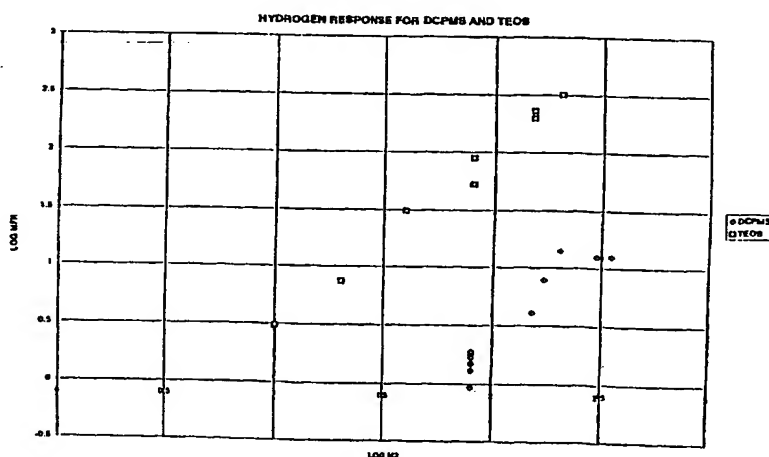
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(54) Title: HIGH IMPACT, FLEXURAL MODULI POLYMERIC MATERIALS FORMED USING SEQUENTIAL DONORS



(57) Abstract

A method of forming high impact copolymer having a high degree of crystallinity and a melt flow rate of at least 10 to 150. The method preferably comprising: subjecting the α -olefin monomer to an initial polymerization, in the presence of a first electron donor material and a first catalyst to form a polymer product; subjecting the polymer product to a subsequent polymerization, in the presence of a second electron donor material and a second catalyst, thereby forming the α -olefin homopolymer; wherein the second donor material is more stereoregulating than the first electron donor material and the second electron donor material dominates the first electron donor material; and polymerizing a copolymer in the presence of the α -olefin homopolymer, thereby forming a high impact copolymer. The first and second catalysts may be the same or different. The copolymer portion of the high impact copolymer will have an unexpected high amorphous phase content.

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APPLICATION FOR U.S. PATENT**HIGH IMPACT, FLEXURAL MODULI POLYMERIC MATERIALS
FORMED USING SEQUENTIAL DONORS**

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FIELD OF THE INVENTION

This invention relates to novel high impact, high flexural moduli polymeric materials, i.e., in situ polymerized polypropylene homopolymers and polypropylene copolymers, formed by a sequential polymerization process in which a different
10 electron donor material is used during the initial and subsequent polymerization steps. In particular, the present inventors have discovered that the second donor material must be more stereoregulating than the first electron donor material and the second electron donor material must also dominate the first electron donor material in order to form in situ polymerized homopolymers and copolymers which
15 exhibit unusually good balances of impact resistances and flexural strengths.

BACKGROUND OF THE INVENTION

The physical properties of homopolymers and copolymers of propylene formed by typical Ziegler-Natta polymerization are highly dependent on the
20 stereoregularity of the polymer itself. Highly stereoregular polymers are crystalline, provide a desirable high flexural moduli and are formed with a suitable choice of electron donor. These highly crystalline polymers also display high melting points, but innately exhibit low melt flow rates (MFR) that render them unsuitable for applications that require high processing rates, such as in injection
25 moldings, oriented films and thermobound fibers. Further, conventional polypropylene homopolymer and copolymer products formed from highly crystalline polypropylenes lack sufficient impact resistance.

The addition of various electron donor materials to Ziegler-Natta catalysts has been known to influence the degree of stereoregularity in polypropylene
30 homopolymers and copolymers. Generally, a single base catalyst (e.g., a magnesium chloride supported base Ziegler-Natta catalyst) can be used in

combination with any number of electron donor materials, each of which, or combination of which, will lead to a specific level of stereoregularity and MFR. One of the properties of electron donors is that the polypropylene MFR, at the same reactor hydrogen level, decreases with increasing polypropylene stereoregularity caused by the donor. Additional hydrogen is required to reach desirable MFRs when highly stereoregulating donors are employed. This relationship between stereoregularity and MFR poses a problem in processes that have hydrogen pressure limitations. In those processes where the desirable hydrogen pressure cannot be reached, a more hydrogen responsive donor material must be used. Such donor materials, however, lead to the formation of less stereoregular polypropylenes with more amorphous polypropylene by-products that produce polypropylenes which lack sufficient flexural moduli. Thus, processes that have hydrogen pressure limitations pose a problem because the final achievable MFR will be determined by the choice of electron donor, which in turn determines the level of polypropylene stereoregularity in the final product.

Therefore, it would be highly desirable to synthesize homopolymers and copolymers in an in situ polymerization process to make high impact copolymers (ICP) that have both high flexural moduli and high MFRs. The present inventors have discovered that the sequential additions of electron donor materials in polymerization reactors connected in series is required to achieve polymers at higher MFRs and at higher levels of crystallinity, where one type of donor is placed in the first reactor and a second type of donor is placed in the second (or subsequent) reactor. It has been found by the present inventors that the sequential use of the two donors broadens both the molecular weight distribution and the compositional distribution of the homopolymer components and provides a more crystalline homopolymer having product characteristics closer to the same polymer formed in the presence of the more stereoregulating donor material by itself. That is, the crystallinity and flexural moduli of the resulting in situ polymerized ICP are higher than expected from the weighted average of the two independent donor products, but the final MFR can be predicted from the weighted average of the independently produced donor products.

The present inventors have also discovered that the choice of electron donor materials affects the downstream ethylene-propylene (E/P) copolymer components produced in an impact copolymer (ICP) process where one or more gas phase reactors are placed downstream from the series of polypropylene homopolymer reactors. That is, the present inventors have unexpectedly discovered that if a combination of donors are selected where the higher stereoregular donor dominates over the lesser stereoregular donor, then the nature of copolymer produced downstream from the homopolymer reaction stage is desirably affected only by the higher stereoregulating donor.

SUMMARY OF THE INVENTION

Novel high impact copolymer in situ polymerized materials (e.g., polypropylene in combination with poly(ethylene-co-propylene)) with substantial degrees of crystallinity and high MFRs can be produced by sequentially adding first and second electron donor materials to a first and second (or subsequent) of a series of reactors, respectively; provided that the second electron donor material is more stereoregulating than the first electron donor material and provided that the second electron donor material dominates the first electron donor material.

A method is presented for forming in situ polymerized homopolymer components that have a broad molecular weight distribution and displays a high flexural moduli indicative of a highly crystalline, isotactic polymer, concurrently with a high MFR. Previously, high MFRs were exhibited only by lesser stereoregular polymers having a higher amorphous content. The method includes the subjection of an α -olefin (e.g., propylene, 1-butene, 1-pentene, 1-hexene, etc.) to an initial polymerization in a first reactor, in the presence of a first electron donor material and a supported Ziegler-Natta catalyst, thereby forming a polymer reaction product and subsequently continuing the polymerization of the polymer reaction product in a second reactor, in the presence of a second and different electron donor material with the same Ziegler-Natta catalyst provided that the second donor material is more stereoregulating than the first electron donor material and provided that the second electron donor material dominates the first

electron donor material. The unique homopolymers formed in accordance with the sequential donor process set forth immediately above are subjected to a further polymerization stage with the same catalyst system where in situ polymerized poly(ethylene-co-propylene)s are formed, thereby creating a high impact copolymer (ICP) that exhibits a superior balance of flexural moduli and impact resistance with the appropriate choice of sequential electron donor materials.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a graph plotting MFR versus hydrogen pressure for tetraethoxysilane (TEOS) and dicyclopentyl dimethoxysilane (DCPMS) electron donors;

Fig. 2 is a graph plotting MFR versus the level of DCPMS in polymerizations using mixed (1) TEOS/DCPMS and mixed (2) PTES/DCPMS donors at a constant hydrogen level of 150 psig;

Fig. 3 is a graph plotting heats of fusion versus the level of DCPMS in polymerizations using mixed TEOS/DCPMS donors at a constant hydrogen level of 150 psig;

Fig. 4 is a schematic depicting stereoregularity (meso run length (MRL)) and its distribution with sequential and single donors;

Fig. 5 is a graph plotting weight % xylene solubles versus 1% Secant Flexural Modulus for both single and sequential donors;

Fig. 6 is a graph plotting weight % xylene solubles versus 1% Secant Flexural Modulus comparing the effect of nucleation on a polymer formed with a single electron donor and a polymer formed with sequential donors;

Figs. 7a and 7b are bar graphs comparing the Gardner Impact strengths of a pigmented polymer formed with a single electron donor and a pigmented polymer formed with sequential donors at both room temperature (i.e., 25°C) and at -29°C, respectively; and

Fig. 8 is a graph plotting the total copolymer weight % ethylene versus the weight % amorphous ethylene/propylene copolymer in high impact polypropylene copolymers polymerized in the presence of a single electron donor and sequential electron donors.

DETAILED DESCRIPTION OF THE INVENTION

The homopolymer components of the in situ polymerization of polypropylene and poly(ethylene-co-propylene) of the present invention possess a broad molecular weight distribution and simultaneously display high flexural moduli, normally associated with highly crystalline polymers, and a high melt flow rate (MFR), normally associated with less stereoregular polymers. These novel homopolymer components are formed in a process where, for example, propylene is sequentially subjected to an initial polymerization in the first series of reactors and in the presence of a Ziegler-Natta catalyst and a first electron donor material. This polymerization is continued in a second reactor where a subsequent or second polymerization reaction occurs in the presence of the same Ziegler-Natta catalyst but with a second electron donor material. The second electron donor material should be more stereoregulating than the first electron donor material. The second electron donor material should also dominate the first electron donor material.

The Ziegler-Natta catalyst useful in the practice of the present invention is a solid titanium supported catalyst system described in US-A-4990479 and US-A-5159021. Briefly, the Ziegler-Natta catalyst can be obtained by: (1) suspending a dialkoxy magnesium compound in an aromatic hydrocarbon that is liquid at ambient temperatures; (2) contacting the dialkoxy magnesium-hydrocarbon composition with a titanium halide and with a diester of an aromatic dicarboxylic

acid; and (3) contacting the resulting functionalized dialkoxy magnesium-hydrocarbon composition of step (2) with additional titanium halide.

The Ziegler-Natta co-catalyst is preferably an organoaluminum compound that is halogen free. Suitable halogen free organoaluminum compounds are, in particular, branched unsubstituted alkylaluminum compounds of the formula AlR_3 , where R denotes an alkyl radical having 1 to 10 carbon atoms, such as for example, trimethylaluminum, triethylaluminum, triisobutylaluminum and tridiisobutylaluminum. Additional compounds that are suitable for use as a co-catalyst are readily available and amply disclosed in the prior art including US-A-4,990,477, which is incorporated herein by reference. The same or different Ziegler-Natta catalyst(s) can be used in both the initial and subsequent polymerization steps.

Electron donors are typically used in two ways in the formation of Ziegler-Natta catalysts and catalyst systems. An internal electron donor may be used in the formation reaction of the catalyst as the transition metal halide is reacted with the metal hydride or metal alkyl. Examples of internal electron donors include amines, amides, ethers, esters, aromatic esters, ketones, nitriles, phosphines, stilbenes, arsines, phosphoramides, thioethers, thioesters, aldehydes, alcoholates, and salts of organic acids. In conjunction with an internal donor, an external electron donor is also used in combination with a catalyst. External electron donors affect the level of stereoregularity and MFR in polymerization reactions. External electron donor materials include organic silicon compounds, e.g. tetraethoxysilane (TEOS) and dicyclopentydimethoxysilane (DCPMS). Internal and external-type electron donors are described, for example, in US-A-4,535,068, which is incorporated herein by reference. The use of organic silicon compounds as external electron donors are described, for example, in U.S. Patent Nos. 4,218,339, 4,395,360, 4,328,122 and 4,473,660, all of which are incorporated herein by reference. The preferred electron donors of the present invention are external electron donors used as stereoregulators, in combination with Ziegler-Natta catalysts. Therefore, the term "electron donor", as used herein refers specifically to external electron donor materials.

The external electron donor acts to control stereoregularity, which affects the amount of isotactic versus atactic polymers. The more stereoregular isotactic polymer is more crystalline, which leads to a material with a higher flexural modulus. Highly crystalline, isotactic polymers also display lower MFRs, as a consequence of a reduced hydrogen response during polymerization. The stereoregulating capability and hydrogen response of a given electron donor are directly and inversely related. The DCPMS donor has a substantially lower hydrogen response than the TEOS donor, but produces a significantly higher level of stereoregularity than TEOS. Because DCPMS is more stereoregulating, it will, at an equal reactor hydrogen pressure, provide a higher level of crystallinity and lower MFR than the lesser stereoregulating TEOS donor.

In the following examples, two different catalyst formulations, which are used to prepare ICPs with similar compositions, are compared. The first is catalyst A, a magnesium chloride supported, titanium-based Ziegler-Natta catalyst system, with sequential donors in serially connected reactors; TEOS (donor A) is used in the first reactor and DCPMS (donor C) in the second reactor. The second catalyst B, is also a magnesium chloride supported, titanium-based Ziegler-Natta catalyst system, with the single cyclohexylmethyldimethoxysilane (CMMS) electron donor B in both reactors. The average level of isotactic polypropylene stereoregularities for these two catalysts are similar as measured by the average *meso* run lengths (MRL) of the in situ produced polypropylene homopolymers. The MRL is determined from the *[mmmr]* fraction from ¹³C NMR data and is given in Table 1 for these two catalyst formulations.

$$\text{MRL} = 2/[\text{mmmr}]$$

(See *Macromolecules* 1997, 30, 803, which is incorporated herein by reference.)

Table 1
(ISOTACTIC POLYPROPYLENE COMPONENT
STEREOREGULARITIES OF SINGLE (Catalyst B/CMMS) AND
SEQUENTIAL DONORS (Catalyst A/TEOS/DCPMS) PRODUCED ICPS)

ICP #	AVERAGE MESO RUN LENGTHS	
	SINGLE DONOR	SEQUENTIAL DONOR
1	223	224
2	200	199
3	180	196
4	235	209
6	240	
6	207	
7	223	
8	179	
9	191	
10	197	
11	197	
12	217	

The donors, TEOS, CMMS and DCPMS produce different levels of stereoregularities when used independently with either of the above catalysts to produce isotactic polypropylene. With Catalyst A, the following stereoregularities have been observed independently with the TEOS, CMMS and DCPMS donors.

Table 2
(Average Meso Run Lengths Observed for Different Single Donors with Catalyst A)

	TEOS	CMMS	DCPMS
MRL	150-180	200	400

A range of MRL values is given for the TEOS donor because the level of stereoregularity of the TEOS donor will also rise with increasing levels of hydrogen; whereas the CMMS and DCPMS donors produce stereoregularities that are less dependent on hydrogen concentration.

Both the compositional and molecular weight distributions of the polypropylene homopolymer components will be broader with the sequential donors over that obtained with the single donor. The average MRLs are both lower and higher for the individual sequential donors, TEOS and DCPMS, respectively, over that for the CMMS donor, as seen in Table 2. Consequently, the breadth of polypropylene stereoregularity will be wider for the sequential donors, even when the *average* stereoregularity is the same for sequential versus single donor polymers, as shown in Table 1. A similar argument holds true for the molecular weight distribution. The MFRs are both lower and higher for the individual TEOS and DCPMS donors, respectively, over the CMMS donor at the same hydrogen level. A 35/65 blend of a 22 MFR homopolymer and a 160 MFR homopolymer, having a blended MFR of 80, will have a broader MWD than an 80 MFR homopolymer made with a single donor and the same catalyst system.

EXAMPLE 1

At 150 psig (1.13 MPa) hydrogen and in the presence of Catalyst A, the use of TEOS as an electron donor led to an MFR of 214 dg/min., a melting point (M.P.) of 157.9°C and a heat of fusion of 108.7 J/g. To the contrary, the same molar concentration of DCPMS electron donor resulted in a MFR of only 4.1, a M.P. of 163.5°C and a heat of fusion of 110.2 J/g in the presence of Catalyst A and a hydrogen pressure of 150 psig (1.13 MPa). Fig. 1 plots MFR versus hydrogen pressure for TEOS and DCPMS electron donors. The data is given in Table 3 below.

Table 3
(HYDROGEN PRESSURE VERSUS MFR FOR ELECTRON DONORS,
TEOS AND DCPMS)

H₂	DCPMS	TEOS
psig	MFR(dg/min)	MFR(dg/min)
10		3.1
20		7.4
40		31.2
40		
80	1.8	53.2
80	1.7	89.2
80	1.3	
80	1.9	
80	1.5	
80	0.93	
80	1.5	
150	4.1	197
150		229
170	7.8	
200		321
300	12.5	
350	12.5	

5 Additionally, the hydrogen response of a donor controls molecular weight of the polymer produced. The TEOS electron donor material exhibited a high hydrogen response leading to a low molecular weight polymer product, while the DCPMS electron donor material exhibited a low hydrogen response leading to a high molecular weight polymer product.

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EXAMPLE 2

15 The tendency of one donor to dominate can be determined by examining the MFR and final crystallinity of the polyolefin produced with a mixture of the two donors at different relative concentrations. In plots of MFR (Fig. 2) and heats of fusion, i.e., as a measure of crystallinity, (Fig. 3) versus the level of DCPMS in polymerizations of propylene using mixed TEOS/DCPMS at a constant hydrogen pressure of 150 psig (1.13 MPa), the dominance of DCPMS over TEOS is clearly established. When the TEOS/DCPMS mixture contains only 10% DCPMS, both

the resulting MFR and heat of fusion are the same or better than those achieved with DCPMS alone. A complete set of data corresponding to Figs. 2 and 3 are provided in Tables 4 and 5, respectively. Also included in Fig. 2 is an example of two mixed donors that show an example where neither donor has a dominating effect. Propyltriethoxy silane (PTES) and DCPMS were used. In this case the MFR closely follows what one might expect of such a mixture, an MFR close to the average of the two donors.

Table 4

(DOMINANCE OF DCPMS OVER TEOS AND NON-DOMINANCE OF DCPMS OVER PTES: MFR VERSUS % DCPMS IN A MIXTURE OF TEOS/DCPMS AND PTES/DCPMS AT A CONSTANT HYDROGEN PRESSURE OF 150 PSIG)

% DCPMS (remainder TEOS)	TEOS/DCPMS MFR	PTES/DCPMS MFR
0	197	59
0	229	
5	10	
10	4.4	40
16	2.4	
25	4.5	27
30	8.7	
50	4.4	11
50	2.1	
50	6.4	
50	4.5	
75	2.6	
100	4.1	4.1

Table 5
(DOMINANCE OF DCPMS OVER TEOS: HEATS OF FUSION VERSUS
% DCPMS IN A MIXTURE OF TEOS/DCPMS AT A CONSTANT
HYDROGEN PRESSURE OF 150 PSIG)

% DCPMS	ΔH (J/g)	MFR
0	107	229
5	108	10
10	113	4
30	114	9
50	113	6
75	115	3
100	110	4

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EXAMPLE 3

In accordance with a preferred embodiment according to the present invention a propylene homopolymer may be formed using a sequence of polymerization reactions. In the initial polymerization reaction, 625 grams of propylene are polymerized to form 320 grams of polypropylene in the presence of 0.008 grams of Catalyst A and 0.0416 grams of a relatively weak stereoregulating electron donor (TEOS). The resulting propylene homopolymer has a moderate stereoregularity as measured by ΔH_f and an MFR of 160. The reaction mixture of the initial polymerization reaction is then passed to a second reactor where further polymerization is conducted in the presence of 0.0456 grams of a more stereoregulating, dominant electron donor (DCPMS). The TEOS from the first polymerization passes to the second stage so that the further polymerization is conducted in the presence of a mixture of TEOS and DCPMS in a weight ratio of one to one. However, since the DCPMS dominates the TEOS, 50% of the polymer created in the second reactor closely resembles a polymer formed in the presence of DCPMS alone. The second reactor polymerization produces a higher isotactic (MRL of approximately 400), lower MFR (22) polymer which leads to a blended MFR of 80 and an average MRL of 200. Each of the first and second reactors can be, for example, a bulk liquid slurry stirred tank reactor.

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Using the same hydrogen content in each of the reactors, the final, average MFR of a polypropylene homopolymer exiting the second reactor is nominally one half the MFR of the product leaving the first reactor. The deblened MFR (i.e., a calculated MFR of the component product from the second reactor) of a polypropylene produced in the second reactor is substantially lower than the average MFR of the homopolymer residing in the first reactor. As shown in Table 6, the MFR in the first reactor is 160 using TEOS as the electron donor material and the blended MFR in the second reactor is 80 using DCPMS as the electron donor material. The deblened MFR in the second reactor is calculated to be 22, using the equation below and wherein $w_1 = 0.649$ and $w_2 = 0.351$ are the production splits in weight fractions in reactors 1 and 2, respectively.

$$\log(\text{MFR}_{\text{reactor 2}}) = (\log(\text{blended MFR}_{\text{reactor 2}}) - w_1 \log(\text{MFR}_{\text{reactor 1}})) / w_2$$

TABLE 6

MFR IN FIRST REACTOR (TEOS)	AVERAGE MFR IN SECOND REACTOR (DCPMS)	DEBLENDED* MFR IN SECOND REACTOR (DCPMS)
160	80	22
140	70	14
80	27	2.4
60	23	4.9

* Calculated MFR in the second reactor.

Once again, the sequential addition of donors leads to a broadening of both the molecular weight distribution and the chiral or stereoregularity distribution of the resulting polypropylene homopolymers. If the stereoregulating capabilities of the donors that produce the high MFR (donor A, e.g., TEOS) and low MFR (donor C, e.g., DCPMS) homopolymers have the following relationship to the single donor that produced independently the median MFR (donor B, e.g., CMMS) homopolymer,

Donor C > Donor B > Donor A
(More Stereoregular → Less Stereoregular)

then the chiral or stereoregularity distribution of the in situ blend will be broader for the sequential donors C and A. Such a broadening of the chiral distribution is illustrated in Fig. 4. Correspondingly, the donor hydrogen responses, at the same hydrogen concentration, that obey the following MFR relationships

$$\text{Donor C} < \text{Donor B} < \text{Donor A}$$

(Lesser H₂ Response → Greater H₂ Response)

will lead to a broader MWD for the sequential donors than the single donor.

The stereoregularity of the propylene homopolymer formed as set forth above ranges from moderate, an average of 150-180 MRL, for the TEOS produced polypropylenes to an average of approximately 400 MRL for the DCPMS produced polypropylenes. Each of these polypropylene components has a distribution surrounding its average stereoregularity. Each of these distributions also incrementally increase in stereoregularity with incremental increases in molecular weight. It has been demonstrated through fractionation studies that the stereoregularities of isotactic polypropylenes, produced with a supported Ziegler-Natta catalyst in conjunction with an electron donor, increase with increasing molecular weight. (See *Polymer* 1994, 25, 2636, which is incorporated herein by reference). The approximately 400 MRL component will have molecules in the upper end of the stereoregular distribution that have MRLs of over 1000. The presence of this high molecular weight, highly stereoregular component leads to a higher flexural modulus than observed for polypropylenes with the same average stereoregularity but with a more narrow distribution. The primary reason for this higher flexural modulus is that the high molecular weight, highly isotactic components crystallize first, and then serve as a template for the lesser stereoregular polypropylenes during crystallization.

The polypropylene crystallinities prepared with the CMMS donor and with the sequential TEOS/DCPMS donor system are therefore significantly different, in spite of similar average polypropylene stereoregularities and similar E/P copolymer

contents. It is well known to those skilled in the art that observed flexural moduli are a direct function of the level of crystallinity. Evidence for the differences in breadths of the stereoregularity distributions causing different crystallinities is apparent from the higher 1% secant flexural moduli provided by the ICPs produced with the sequential TEOS/DCPMS donors, as shown in Fig. 5 and given in Table 7. The flexural moduli data are presented as a function of xylene solubles content; this xylene soluble fraction contains both the amorphous component of the poly(ethylene-co-propylene) copolymer and atactic polypropylene component of the homopolymers and copolymers. Both of these components soften the polypropylene matrix, thereby reducing the flexural modulus. The E/P copolymer, however, contributes to much improved impact strengths, which is the purpose for preparing the in situ blend.

TABLE 7

**1% SECANT FLEXURAL MODULI OF UN-NUCLEATED ICPS AT
GENERALLY THE SAME MESO RUN LENGTH PREPARED BY
SINGLE AND SEQUENTIAL DONORS AS A FUNCTION OF XYLENE
SOLUBLES CONTENT (a-PP + a-E/P)**

ICP #	SEQUENTIAL DONORS		SINGLE DONOR	
	% Xylene Solubles	1% Secant Flexural Modulus	% Xylene Solubles	1% Secant Flexural Modulus
1	7.16	219		
2	8.14	187		
3	8.35	206		
4	8.39	215	8.41	188
5	8.56	219		
6	8.79	190		
7	8.87	190		
8	9.24	216	9.06	177
9	9.46	205		
10	9.59	198		
11	9.80	211	10.00	187
12	10.48	172		
13	11.09	186	11.06	172
14	11.50	208		
15	11.99	194	11.92	150
			11.92	170
16	12.25	190		
17	13.95	192	13.65	168
18	14.24	198		
19	14.45	188	14.63	164
			15.35	173
			15.82	143
20	16.65	184	16.23	159
			16.56	165
21	16.91	177		
22	17.36	181		
23	17.46	168		
24	19.89	172		
25	22.66	144		
26	24.02	139		
27	26.65	118		
28	27.10	118		

The 1% secant flexural moduli of ICPs prepared with sequential TEOS/DCPMS donors and Catalyst A obey the following relationship:

$$1\% \text{ Secant Flexural Modulus} = -4.43(\text{wt.\% xylene solubles}) + 254.5 \quad (\text{Eq. A})$$

wherein wt.% xylene solubles is the weight percent of the ICP that remains solublized in xylene at room temperature (21-25°C), and signifies the wt.% of the ICP that is totally amorphous and cannot crystallize at room temperature. The amorphous components of an ICP (atactic polypropylene and amorphous ethylene/propylene copolymers) have a negative influence on the flexural modulus, which again is predominantly a function of crystallinity.

The single CMMS donor-produced ICPs, in contrast, exhibited a 1% secant modulus in accordance with the following relationship:

$$1\% \text{ Secant Flexural Modulus} = -3.00(\text{wt.\% xylene solubles}) + 209.5 \quad (\text{Eq. B})$$

These equations were developed for polymers with average meso run length of 200 and are operative for a range of 170-250 average meso run length, as shown in Table 1.

The 1% Secant Flexural Modulus of sequential donor produced ICPs will be at least 5%, preferably 10%, more preferably 15%, most preferably 20% greater than that described by Equation B for a given xylene solubles level (See Fig. 5). These observed differences in 1% secant flexural moduli, given above, are caused by the fact that highly stereoregular, high molecular weight homopolymers influence the crystallization process of polypropylene. The DCPMS component of the sequential TEOS/DCPMS donors leads to polypropylene components with very high stereoregularities that are not produced to the same extent with the CMMS donor, such that the final crystallinity is closer to that produced by the more stereoregulating donor, DCPMS. This allows a higher crystallinity (and resulting higher flexural moduli) than can be provided by a polypropylene having the same overall average stereoregularity that is formed using a single donor with a

lesser breadth of the stereoregularity distribution. At the same time, the observed MFR is a logarithmic average of that produced by the sequential donors, TEOS, which leads to a high MFR and DCPMS, which leads to a low MFR.

5

EXAMPLE 4

A high impact copolymer (ICP) according to the present invention can be formed by polymerizing *in situ*, that is, in the presence of the propylene homopolymer of Example 3 and with the same catalyst system, a copolymer formed from 20 to 80% ethylene and 80 to 20% of propylene in a third (and
10 fourth) reactor, typically a gas phase reactor(s). The composition of the final product is an ICP having between 1 to 50% of an ethylene/propylene copolymer, and 99 to 50% of a propylene homopolymer. The total percent ethylene content of the ICP formed above ranges from 1 to 25% and the ICP has an MFR from 10 to over 100. Conventional ICPs have a MFR of from 0.3 to 100.

15

Polymerization Process for the Synthesis of Impact Copolymer

The continuous polymerization process referred to above as *in situ* polymerization consists of two bulk liquid reactors in series followed by one or more gas phase reactors. Generally, homopolypropylene is polymerized within the
20 bulk liquid reactors followed by ethylene-propylene copolymerization in one or more gas phase reactors. The final product is typically called an "ICP". The donor system in the process could be a single donor such as cyclohexylmethyldimethoxysilane (CMMS) or sequential donors such as tetraethoxy silane (TEOS) and dicyclopentyldimethoxy silane (DCPMS). The
25 concentration of the donor is similar in the two liquid bulk reactors in the case of single donor and different in the case of sequential donors, resulting in either the same MFR polypropylene in the two reactors with a single donor type and completely different MFRs with sequential donors. The resultant polymer is transferred to the gas phase reactor wherein an ethylene-propylene copolymer is
30 polymerized.

Typical Polymerization Conditions for a Single Donor with Catalyst B

The temperatures within the bulk liquid reactors and gas phase reactor is 158°F (70°C). The hydrogen and triethylaluminum (TEAL) concentrations in the first bulk liquid reactor are 3595 ppm and 75 ppm respectively. The CMMS concentration in the liquid bulk reactors is 25 ppm. The hydrogen concentration in the second liquid bulk reactor is 1950 ppm, resulting in a polypropylene MFR of 53 to 55 dg/min. The production splits in the two liquid bulk reactors were 65:35 (first:second). The hydrogen concentration in the gas phase reactor is 55,000 ppm, and ethylene monomer to the ethylene plus propylene monomer ratio is 0.45 and the reactor pressure is 190 psig (1.41 MPa). The ethylene content in the ethylene-propylene copolymer is 57.5 wt.%, and a total rubber level of 14 to 15 wt.%. The final MFR of ICP is 33-37 dg/min.

Typical Polymerization Conditions for Sequential Donors with Catalyst A

The continuous polymerization process is similar to the single donor example, but with some changes in the donor systems in the liquid bulk reactors. The donor systems in this process are called sequential donors, because two different donors are used, namely tetraethoxy silane (TEOS) in the first liquid bulk reactor and TEOS and dicyclopentyldimethoxy silane (DCPMS) in the second bulk liquid reactor. In the first bulk liquid reactor, the donor TEOS produces a high MFR polypropylene, and in the second bulk liquid reactor the combination of TEOS and DCPMS produces a low MFR polypropylene which is attributed to the dominance of DCPMS donor in presence of TEOS.

The hydrogen and triethylaluminum (TEAL) concentrations in the first bulk liquid reactor are 1670 and 57 ppm, respectively. In the second liquid bulk reactor the hydrogen and TEAL concentrations are 1550 and 57 ppm, respectively. The TEOS concentration in the first liquid bulk reactor is 21.4 ppm, resulting in a polypropylene MFR of between 130-140 dg/min, and the concentrations of TEOS and DCPMS in the second liquid bulk reactor are 21.5 and 36.6 ppm, resulting in a de-blended MFR of between 20-22 dg/min or a blended MFR of the two reactors of 69-75 dg/min. The production splits in the two liquid bulk reactors were 65:35

(first:second). The hydrogen concentration in the gas phase reactor is 38,000 ppm, and ethylene monomer to the ethylene plus propylene monomer ratio is 0.35 and the reactor pressure is 190 psig (1.41 MPa). The ethylene in the ethylene-propylene copolymer is 50-55 wt.%, and a total copolymer level of between 15 to 15.4 wt.%. The final MFR of ICP is between 35-38 dg/min.

ICPs formed with the propylene homopolymers of the present invention are superior to ICPs formed with single donor-formed polypropylene for a number of reasons. Ethylene/propylene copolymers produced downstream from sequential donor-prepared polypropylene have both crystalline and amorphous components. (Such polymers are referred to as "bipolymers" and are characteristically produced by Ziegler-Natta catalysts typically used in the highly stereoregular polymerizations of α -olefins). It is the amorphous component of the ethylene/propylene copolymer that is the "rubber-like" copolymer. It was discovered by the present inventors that the ratio of amorphous to crystalline portions of the copolymer is related to the stereoregulating ability of the catalyst system, which is influenced by the choice of electron donor material. The resulting level of crystallinity of a particular copolymer will vary, based upon the electron donor material that is used in the upstream homopolymer polymerization steps. The level of copolymer crystallinity caused by a particular electron donor material is as follows:

TEOS \geq CMMS > DCPMS.

(More Copolymer Crystallinity \rightarrow Less Copolymer Crystallinity)

Because amorphous ethylene/propylene copolymers are required to provide high impact resistance in an ICP, it is highly desirable that these ICPs comprise a high percentage of amorphous copolymer within the bipolymer. DCPMS provides the lowest level of crystalline ethylene/propylene copolymers. However, because of its low hydrogen response, DCPMS can only be used to produce low MFR ICPs. The TEOS/DCPMS sequential donor catalyst system according to the present invention has an excellent overall hydrogen response, which leads to ICPs having MFRs in the range of between 5 to 100. Further, because DCPMS

dominates TEOS, the TEOS/DCPMS sequential donor catalyst system produces
bipolymers as if DCPMS were the only donor. Therefore, the TEOS/DCPMS
sequential donor catalyst system provides the highest possible level of amorphous
copolymer in the bipolymer and at an acceptable level of MFR and homopolymer
crystallinity.

Furthermore, because the highly isotactic components of the polymer
crystallize first, a template is provided for the lesser stereoregular polypropylenes
during subsequent crystallizations leading to undesirable lower flexural modulus.
This behavior causes the lesser stereoregular polymers to be less affected by
external nucleating agents. This becomes important when ICPs are colored with
pigments, which can act as nucleating agents that cause additional crystallization.
Since the amorphous segments of ICPs formed with sequential donor-produced
propylene homopolymers are more resistant to nucleation by pigments, they retain
a better balance of flexural modulus and impact resistance after pigmentation. This
behavior also allows the ICPs of the present invention to be colored with a broader
range of pigments without this deleterious effect, which is critical for many of the
commercial end-use applications for which they may be incorporated, e.g.,
injection molded products.

The examples below further demonstrate the improved nature of materials
formed in accordance with the methods of the present invention, in comparison to
materials formed using methods employing a single electron donor.

As is apparent from the above data, the average stereoregularities of
propylenes produced with a single CMMS donor/Catalyst B and the
TEOS/DCPMS sequential donors/Catalyst A are similar. The average *meso* run
length, which is the average isotactic sequence length between stereo defects is an
excellent measure of polypropylene stereoregularity. The average *meso* run length
for the CMMS donor in combination with Catalyst B was 207; the length of *meso*
runs based on 12 observations ranged from 180 to 240. An average *meso* run of
207 was also observed in ICPs produced with the sequential TEOS/DCPMS donor
system and Catalyst A; based on 4 observations ranging in average *meso* run
Length (MRL) from 180 to 220.

The molecular weight distribution (M_w/M_n) for the single donor system with Catalyst B averaged 3.7 by GPC and ranged from 3.4 to 4.1. The average molecular weight distribution by GPC for the sequential donor system was 3.9, with values ranging from 3.3 to 4.6. Therefore, the molecular weight distribution was slightly higher for the sequential donor formed polypropylene, while the average stereoregularities for the two donor/catalyst systems were similar. This change in molecular weight distribution, although apparently small, was manifested in the processing behaviors of the inventive and comparative ICPs. The peak injection pressure during injection molding was observed to be 6700 psi (46.16 MPa) for the CMMS single donor-produced ICPs. At the same final MFR, the TEOS/DCPMS sequential donor produced ICPs generated a peak injection pressure of only 5900 psi (40.65 MPa). It is well known to those skilled in the art that increasing the breadth of the molecular weight distribution of a polymer will improve processability during injection molding.

EXAMPLE 5

Each of the ICPs formed in accordance with Examples 4, above, were externally nucleated with sodium benzoate. As shown in Fig. 6 and Table 8, the ICPs formed using the sequential TEOS/DCPMS donor system of the present invention are not affected to as great an extent by external nucleating sources (e.g., 12% or less difference) compared with ICPs formed via a single donor system which demonstrate greater than 27% difference.

TABLE 8
1% SECANT FLEXURAL MODULI BEFORE AND AFTER
NUCLEATION OF SINGLE AND SEQUENTIAL DONOR ICPS

	SEQUENTIAL DONORS			SINGLE DONORS*		
	% Xylene Solubles	1% secant Flexural Modulus (kpsi)		% Xylene Solubles	1% secant Flexural Modulus (kpsi)	
		un-nucleated	nucleated		un-nucleated	nucleated
1	19.90	172	192	12.26	155.7	207
2	16.91	177	195	14.71	155.7	197
3	14.6	182	205	13.59	155.7	208
4	16.1	177	200			
5	20.16	172	184			
6	18.57	179	197			
7	16.30	193	210			
8	16.57	166	181			
9	16.70	173	181			
10	16.95	167	184			
11	22.30	157	164			

* The data was averaged from a number of observations of a single grade.

Therefore, the balance between flexural moduli and impact resistance of the ICP formed via a sequential donor system will be better maintained regardless of the addition of nucleating agents and additives that can act as nucleating agents, such as pigments.

EXAMPLE 6

Each of the ICPs formed in accordance with Examples 4 and 5, above, were colored with gray and camel pigments as follows:

The samples for testing were molded on a 75 ton Van Dorn injection molding machine, using a mold with ASTM test specimens (ASTM D3641). The samples with pigments were dry blended in the pellet form prior to injection molding.

The superiority of ICPs formed using the sequential donor system of the present invention in maintaining impact properties after pigmentation compared to ICPs formed from a single donor system is shown by Figs. 7A and 7B, as well as in Table 9 below.

Table 9
(PHYSICAL PROPERTY EVALUATION)

Composition and Property	Sample #									
	1	2	3	4	5	6	7	8	9	10
Sequential Donors(wt.%)	100	98	98	98	98					
Single Donor (wt.%)						100	98	98	98	98
Medium misty grey pigment ¹ (wt.%)		2					2			
Medium misty grey pigment ² (wt.%)			2					2		
Medium camel pigment ³ (wt.%)				2					2	
Medium camel pigment ⁴ (wt.%)					2					2
MFR (dg/min)	35	35	35	35	35	35	35	35	35	35
1% Sec. Flexural Modulus (kpsi)	184	185	187	185	185	208	206	208	206	207
1% Tan. Flexural Modulus (kpsi)	190	191	193	192	190	214	212	215	213	207
HDT @ 66 psi (°C)	107	107	105	106	107	115	114	117	116	119
Gardner @ 23 °C	245	232	236	235	243	243	175	180	199	179
Gardner @ -29 °C	173	157	165	165	173	125	65	94	129	114
Notched Izod @ 23°C (ft-lbs/in)	1.32	1.38	1.33	1.50	1.55	0.86	0.78	0.75	0.84	0.83

1 denotes a carrier resin which is Linear Low Density Polyethylene

2 denotes a carrier resin which is Polypropylene

3 denotes a carrier resin which is Linear Low Density Polyethylene

4 denotes a carrier resin which is Polypropylene

The increased retention of impact properties allows ICPs produced by the sequential donor system of the present invention to be pigmented with a greater variety and quantity of pigments.

EXAMPLE 7

In the ICP process, the catalyst particles bearing the homopolymer component continue downstream to one of more gas phase reactors to produce in situ an ethylene propylene(E/P) copolymer with a predesigned ethylene content.

The E/P copolymer has both a crystalline and an amorphous component, but only the amorphous component makes a significant contribution to the impact properties of the ICP. In spite of the process and choice of magnesium chloride supported Ziegler-Natta base catalyst, the amorphous content of the E/P copolymer will increase as the total copolymer ethylene content diminishes. There can be some control exercised over the amount of amorphous E/P copolymer as a function of total ethylene content through a judicious choice of electron donor, as shown below for the CMMS and DCPMS single donor systems:

Table 10

(% Amorphous Ethylene/Propylene Copolymer
for Single Donors with Catalyst A)

Single Donor	Wt.% Amorphous E/P in total Bipolymer	Wt.% Ethylene in Total Bipolymer
CMMS	75.4	36
DCPMS	81.1	49
DCPMS	84.8	46

Although the DCPMS donor clearly leads to a higher amorphous copolymer content in the bipolymer, it cannot be used alone to produce an ICP because of the severe limitations placed upon the MFR of the polypropylene homopolymer component. The sequential donor concept has been found to alleviate this difficulty because the initial TEOS donor leads to a high MFR, which is averaged, and the DCPMS donor in the second reactor dominates TEOS sufficiently to produce a bipolymer downstream with characteristics more typically associated with that obtained from a single donor DCPMS process. This result is illustrated in Figure 8 and Table 11, below:

TABLE 11
% AMORPHOUS VERSUS % ETHYLENE IN BIPOLYMER AND
CHOICE OF CATALYST/DONORS

#	Sequential Donors		Single Donor		Other ICPs*	
	% E in Bipolymer	% a-E/P in Bipolymer	% E in Bipolymer	% a-E/P in Bipolymer	% E in Bipolymer	% a-E/P in Bipolymer
1	44	82	59	75	56	79
2	41	76	58	75	57	70
3	39	74	62	73	35	77
4	49	83	55	77	64	62
5	50	82	57	75	50	70
6	33	83	58	76	51	70
7	56	78	61	72	50	75
8	53	85	52	74	45	74
9	45	82	72	58	56	70
10	46	82	69	59	52	70
11	49	87	66	72	49	74
12	60	69	68	68	53	78
13	43	86	53	73	50	80
14	38	81	60	67		
15	39	86	56	75		
16	43	85	56	77		
17	47	86	57	77		
18	41	83	63	74		
19	45	91	62	62		
20	48	87	64	60		
21	53	78	62	69		
22	45	77	60	69		
23	54	84	63	72		
24	53	85	59	73		
25	55	83	54	74		
26	54	81	59	74		
27	53	81	65	69		
28	51	80	61	69		
29	52	79	61	70		
30	67	71	60	71		
31	55	73				

TABLE 11 (cont'd)
% AMORPHOUS VERSUS % ETHYLENE IN BIPOLYMER AND
CHOICE OF CATALYST/DONORS

#	Sequential Donors		Single Donor		Other ICPs*	
	% E in Bipolymer	% a-E/P in Bipolymer	% E in Bipolymer	% a-E/P in Bipolymer	% E in Bipolymer	% a-E/P in Bipolymer
32	60	78				
33	60	58				
34	57	85				
35	59	82				
36	59	81				
37	54	84				
38	54	77				
39	57	77				
40	63	81				
41	62	79				
42	55	83				
43	55	79				
44	59	77				
45	58	80				
46	58	79				

* ICPs made from methods other than those of the present invention.

Samples 1 and 2 are ICPs sold by Himont.

Sample 3 is an ICP sold by Amoco Chemical Company.

Samples 4, 9, 10 and 12 are ICPs sold by Mitsubishi Chemical Company, Ltd.

Samples 5 and 6 are sold by Tonen.

Samples 7, 8 and 11 are ICPs sold by Aristech.

Sample 13 is an ICP sold by Genesis.

Fig. 8 plots the total copolymer wt.% ethylene against wt.% amorphous copolymer for ICPs produced by sequential addition of electron donors (TEOS/DCPMS) and single (CMMS) donors, respectively. For comparison purposes, Fig. 8 also has data, i.e., samples 1-13, generated from commercially available ICPs made by processes different from that of the present invention. The majority of ICPs produced by the sequential addition of donors contained more than 80 wt.% amorphous copolymer. Fig. 8 further demonstrates the previous statement that the wt.% amorphous copolymer increases as the total copolymer wt.% ethylene decreases. Even at a 60 wt.% ethylene content (total copolymer

wt.%), the amorphous copolymer content was 75 to 80% for the sequential donor-prepared ICP, as opposed to only 70% for the single CMMS donor-prepared ICPs. The other ICPs of samples 1-13 give results similar to that observed for a single donor system. Fig. 8 also shows that the wt.% amorphous copolymer for the sequential TEOS/DCPMS is similar to that produced by use of a DCPMS donor, alone. The increased wt.% amorphous copolymer for the sequential donor-produced ICPs leads to a better balance between flexural moduli and impact strength. A sodium benzoate-nucleated ICP with 12 wt.% xylene solubles and prepared with a single CMMS donor and Catalyst B displays a 1% secant flexural modulus of 210 ± 5 (kpsi) and a Gardner impact strength at -29°C of 120 ± 26 inch lbs. The corresponding nucleated ICP prepared by sequential addition of electron donors and 16 wt.% xylene solubles displays a 1% secant flexural modulus of 184 ± 5 (kpsi) and a Gardner impact strength at -29°C of 168 ± 11 inch lbs. The following equation can be used to predict 1% secant flexural moduli for nucleated ICPs prepared with the single donor system:

$$1\% \text{ Secant Flexural Modulus (kpsi)} = -4.90 (\text{wt.\% xylene solubles}) + 248.3 \quad (\text{Eq. C})$$

The following results are obtained for 12 and 16% xylene solubles:

Table 12

% Xylene Solubles	Predicted 1% Secant Flexural Modulus (kpsi)	Observed 1% Secant Flexural Modulus (kpsi)
12	190	210 (single donor)
16	170	184 (sequential donor)

This exercise demonstrates that the 1% secant flexural moduli are comparable for the nucleated ICPs prepared with single and sequential donors, respectively.

The impact strengths, however, differ substantially with the sequential donor prepared ICP having a Gardner Impact Strength at -29°C of 168 inch

pounds, while the comparable single donor system has a Gardner Impact Strength at -29°C of only 120 inch pounds. This difference in impact strengths is also demonstrated in Table 9. The sequential donor catalyst system allows more bipolymer to be incorporated into an ICP with an accompanying higher amount of amorphous E/P without sacrificing the 1% secant flexural modulus.

The amorphous content of the bipolymer formed according to the present invention may be between 75-100%, preferably between 80-100%, at an ethylene content of 60% or greater in the bipolymer. At lower ethylene content the amorphous content will be between 82-100%, preferably between 84-100%, more preferably between 86-100%. In another embodiment the amorphous content of the bipolymer is between 82-98%, preferably 84-98%, more preferably 85-98%, and most preferably 86-98%.

Physical Property Measurements

• Melt Flow Rate (MFR)

MFR is measured according to ASTM D1238 test method, at 230°C and 2.16 kg load, and is expressed as dg/min or g/ 10 min.

• Flexural Modulus

The flexural modulus is obtained according to ASTM D790A, with a crosshead speed of 1.27 mm/min, and a support span of 50.8 mm, using an Instron machine.

• Gardner Impact Strength

The Gardner Impact Strength was measured according ASTM D3029, Method G, Procedure GC, at -29°C and 23°C, on 90 mm diameter and 3.175 mm thickness disks.

• Heat Deflection Temperature

The heat deflection temperature (HDT) is measured according to ASTM D 648, and under a load of 66 psi, using the equipment made by Ceast Corp.,

- **Notched Izod Impact Strength**

The room temperature notched izod impact strength (RTNI) is measured according to ASTM D256 test method. The impact strength equipment is made by
5 Empire Technologies Inc.

- **Procedure for Xylene Solubles and Insolubles of Impact Copolymers of Polypropylene**

10 The procedure consists of pressing polymer resin in the form of pellets into a pad by melt pressing at 210°C for 1 minute and cooling to room temperature in 1 minute. A 2 gram sample from the pad is weighed and dissolved in xylene at 135°C. After the polymer is dissolved completely, the heat source is removed and allowed to cool spontaneously overnight. The precipitated or solidified polymer is filtered, washed thoroughly with xylene, dried and weighed. The solidified portion
15 thus obtained is represented as xylene insolubles. The filtrate containing the soluble polymer is concentrated by removing xylene under vacuum overnight. The polymer thus obtained is washed with a small amount of acetone and dried. The weight of the polymer thus obtained is represented as xylene solubles at room temperature.

20 While preferred embodiments in accordance with the invention have been shown and described, it is to be clearly understood that the same are susceptible to numerous changes apparent to one of ordinary skill in the art. Therefore, the invention should not be deemed to be limited to the details shown and described above, but should be considered to include all changes and modifications that come
25 within the scope of the appended claims.

CLAIMS**We claim:**

1. A method of forming a high impact copolymer comprising:
subjecting an α -olefin monomer to an initial polymerization, in the presence
5 of a first electron donor material and a first catalyst to form a polymer product;
subjecting said polymer product to a subsequent reaction, in the presence of
a second electron donor material and a second catalyst, thereby forming said α -
olefin homopolymer; wherein said second donor material is more stereoregulating
than said first electron donor material and said second electron donor material
10 dominates said first electron donor material; and
polymerizing a copolymer in the presence of said α -olefin homopolymer;
thereby forming said high impact copolymer;
preferably wherein said α -olefin monomer is selected from the group
consisting of: propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-
15 nonene, and 1-decene;
preferably wherein said first and second electron donor materials are any
organic silicon compounds;
2. The method of claim 1, wherein said first electron donor material is
tetraethoxy silane and said second electron donor material is
20 dicyclopentydimethoxysilane, and wherein said copolymer is selected from any
ethylene/ α -olefin copolymer.
3. The method of claim 1, wherein said first and second catalysts are
either the same or different from one another.
- 25 4. The method of any of the preceeding claims, wherein said
copolymer is an ethylene/ α -olefin copolymer having a weight ratio of ethylene to
 α -olefin in an amount between 20:80 to 80:20, and wherein the ethylene content
of said ethylene/ α -olefin copolymer is in the range between 1 to 80 wt.%.

5. A high impact copolymer having a bipolymer component, said bipolymer component being at least 80% amorphous phase with the remainder being crystalline, said copolymer having an overall ethylene content in the range between 60 to 80%.

5

6. The high impact copolymer of claim 5, further having a flexural modulus in the substantial absence of a nucleating agent at least 10% greater than that described by the general equation:

10
$$1\% \text{ secant flexural modulus} = -3.00 (\text{wt.}\% \text{ xylene solubles}) + 209.5$$

wherein wt.% xylene solubles is the wt.% of said high impact copolymer chain which is soluble in xylene at 21-25°C, and wherein said high impact copolymer has a melt flow rate in the range between 10 to 150.

15

7. The copolymer of claim 6, further comprising 2 wt.% pigment and carrier, based on the combined weight of said copolymer, wherein the pigmented copolymer retains at least 95% of the impact resistance of non-pigmented copolymer at both 25°C and -29°C.

20

8. A high impact copolymer comprising an ethylene/ α -olefin copolymer component that contains at least 75% amorphous phase, with the remainder being crystalline, said copolymer having an overall ethylene content is 60% or greater.

25

9. A high impact copolymer which comprises an ethylene/ α -olefin copolymer component that contains at least between 82 to 100 wt.%, preferably between 84 to 100 wt.%, more preferably between 86 to 100 wt.% amorphous phase ethylene- α -olefin and between 0 to 18 wt.%, preferably between 0 to 16 wt.%, more preferably between 0 to 14 wt.% crystalline phase ethylene- α -olefin,

30

wherein the ethylene content in said ethylene/ α -olefin copolymer is 60 wt.% or less.

10. The copolymer of claim 9 further comprises pigment additives, whereby said high impact copolymer maintains a substantially constant Gardner impact at -29°C.

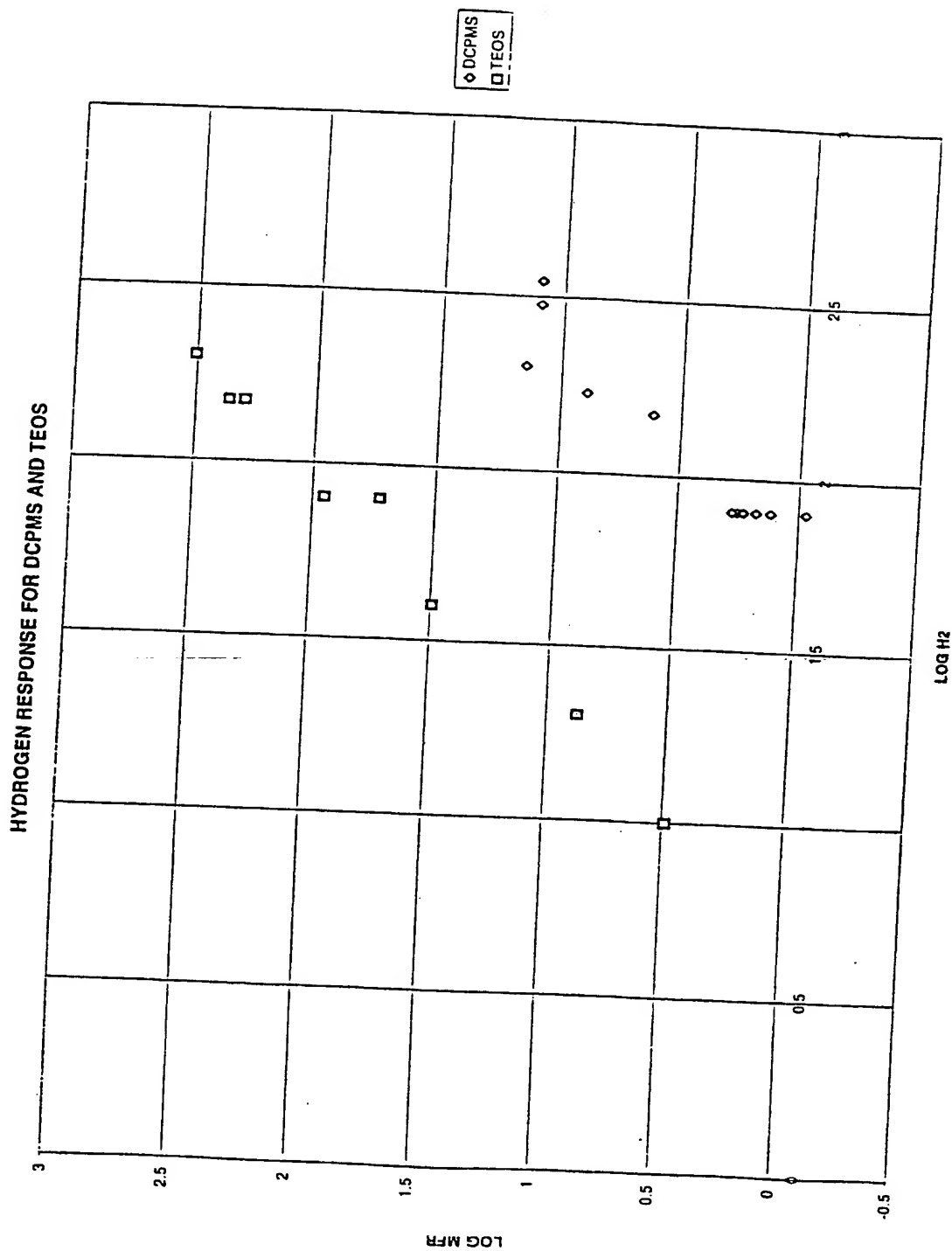
11. The copolymer of claim 9, wherein said high impact copolymer retains 95% or better of its Gardner impact at 25 and -29°C after 2 wt.% pigmentation with carriers of poly(α -olefin) or linear low density polyethylene and with different colors.

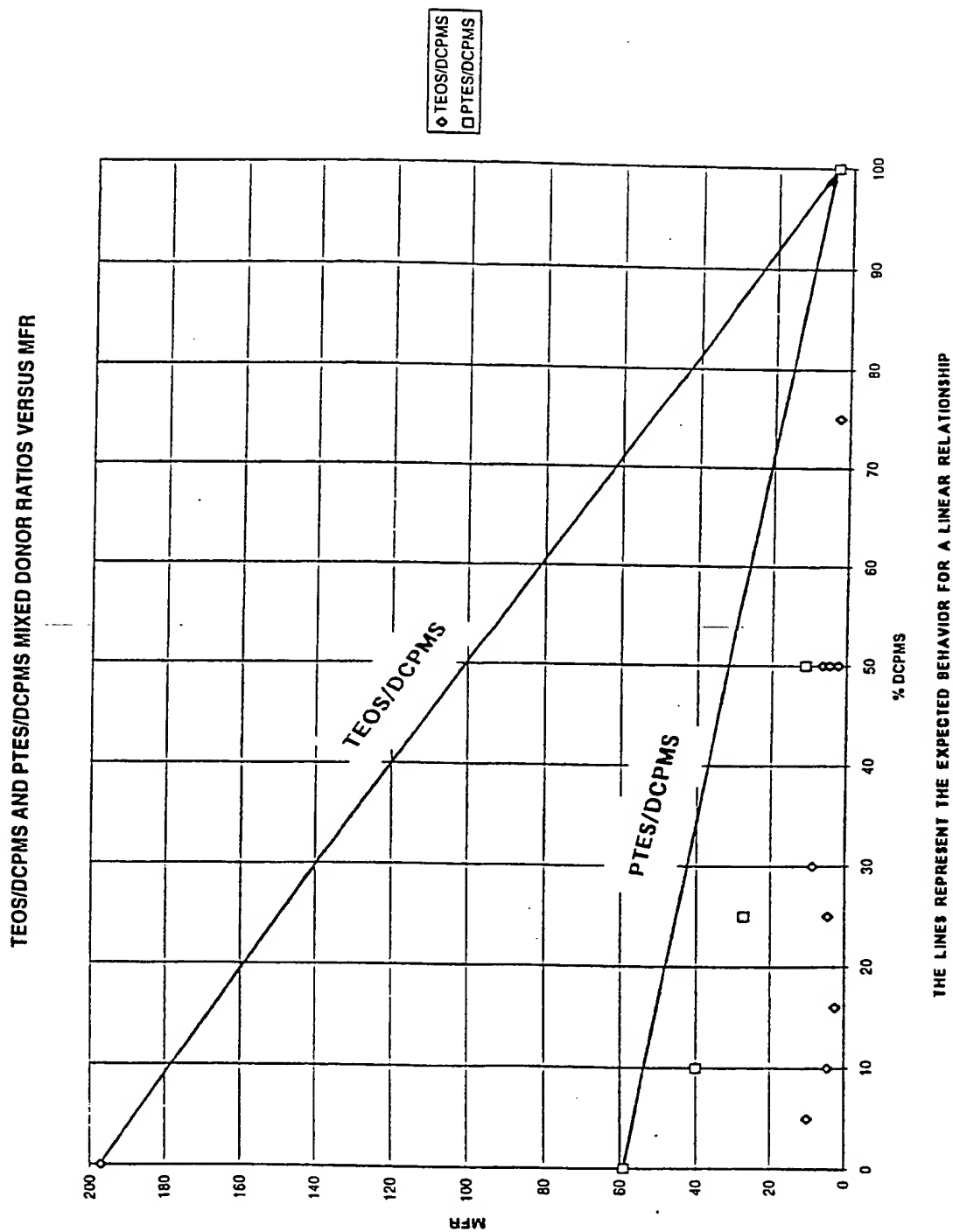
12. The copolymer of claim 9, wherein said high impact copolymer has a flexural modulus in the substantial absence of a nucleating agent, at least 10%, preferably 15% greater than that described by the general equation:

$$1\% \text{ secant flexural modulus} = - 3.00 (\text{wt.\% xylene solubles}) + 209.5$$

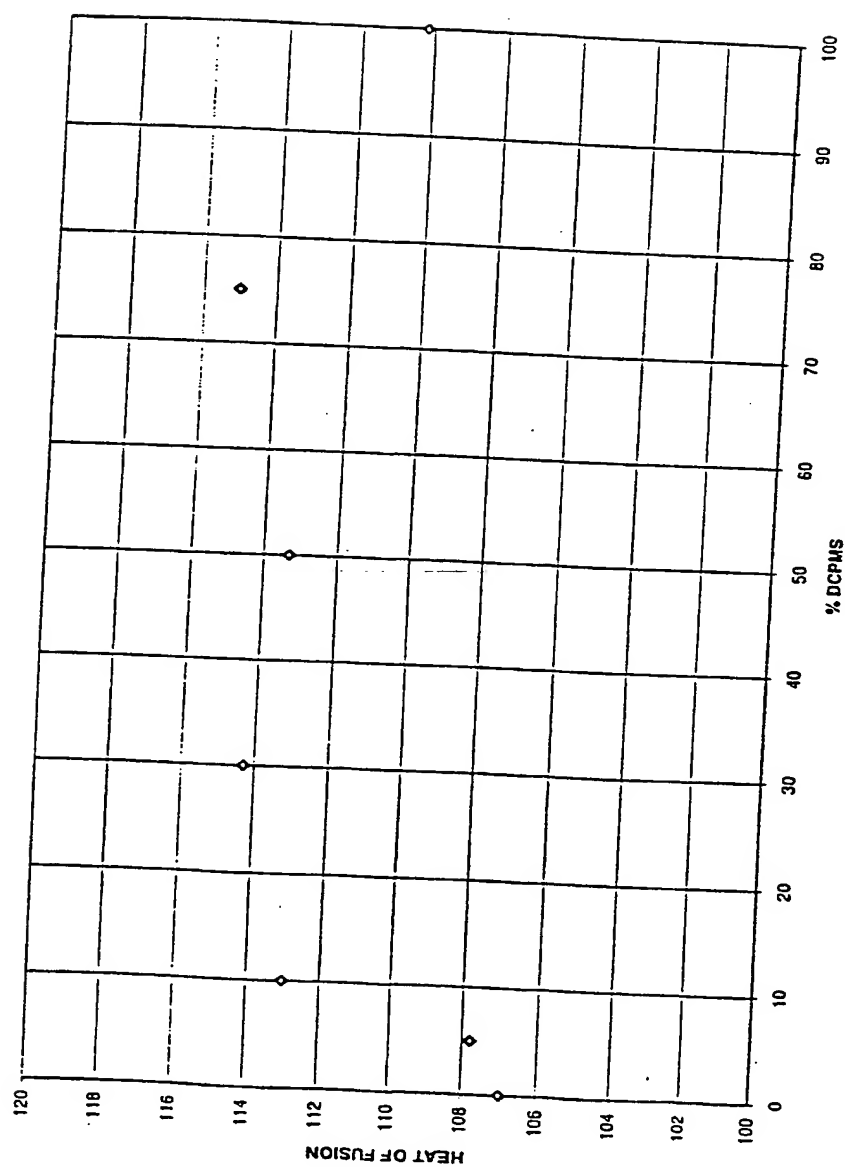
wherein wt.% xylene solubles is the wt.% of said high impact copolymer chain which is soluble in xylene at 21-25°C, and wherein said high impact copolymer has a melt flow rate in the range between 10 to 150; and

preferably, wherein said high impact copolymer includes an ethylene α -olefin copolymer containing at least 82% or greater amorphous phase



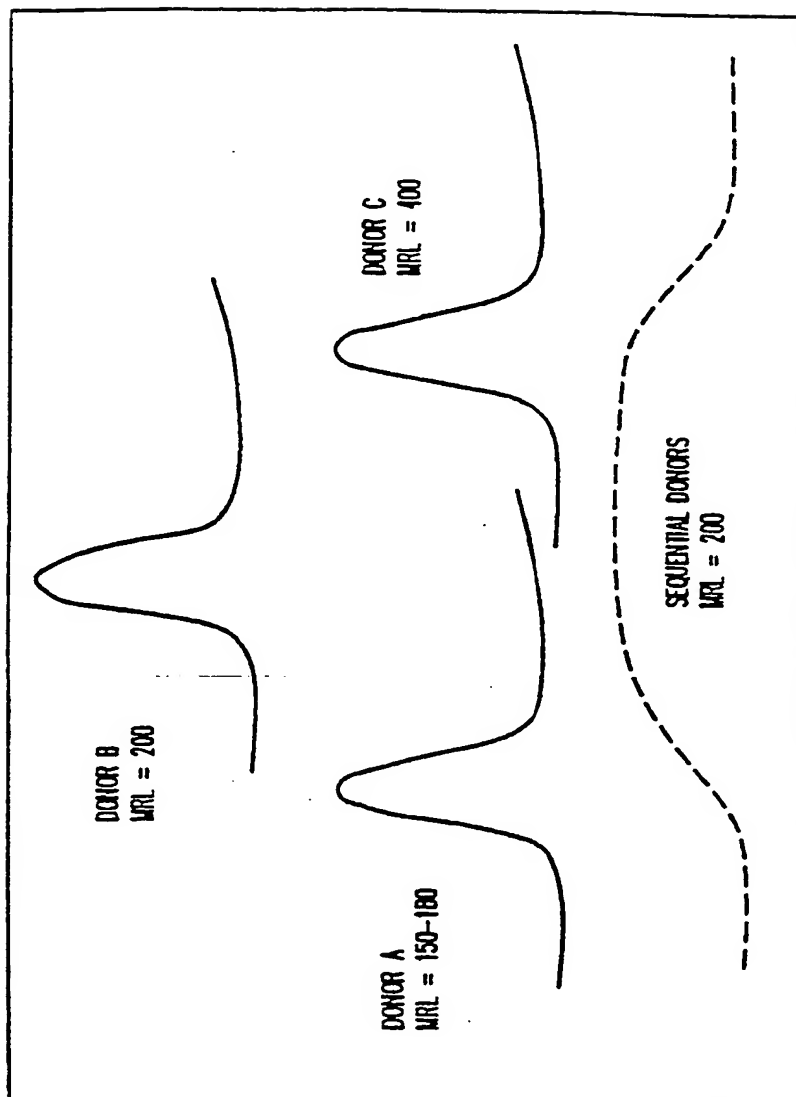


HEAT OF FUSION VS. % DCPMS



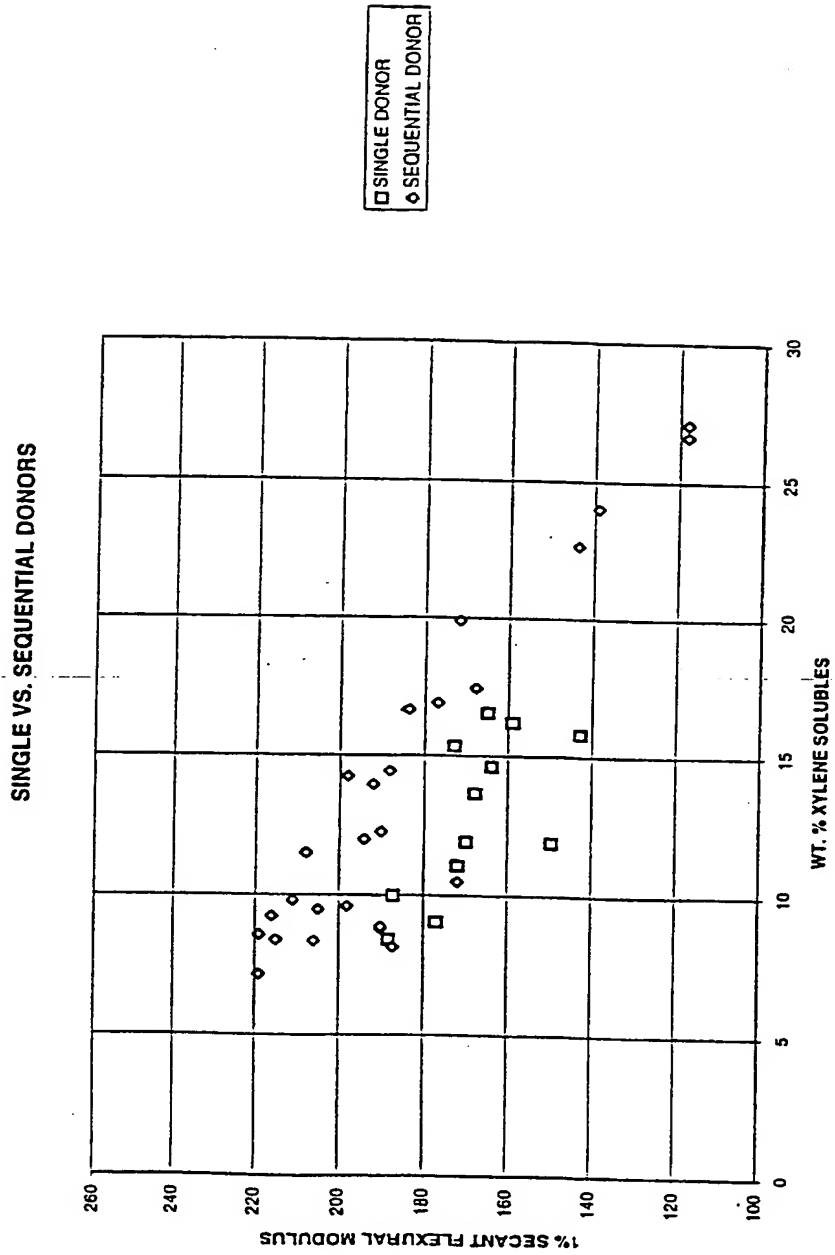
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STEREOREGULARITY AND ITS DISTRIBUTION WITH
SEQUENTIAL & SINGLE DONORS



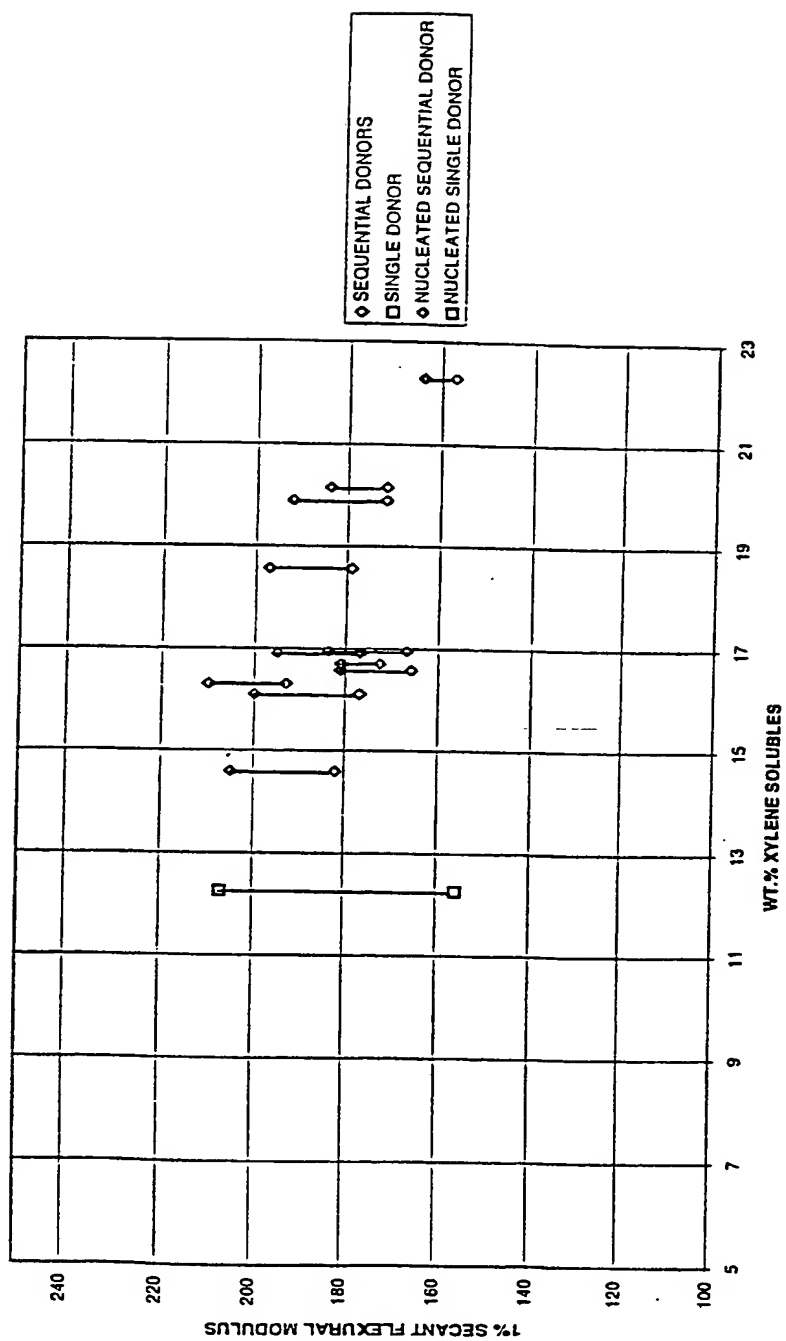
STEREOREGULARITY (MESO RUN LENGTH (MRL))

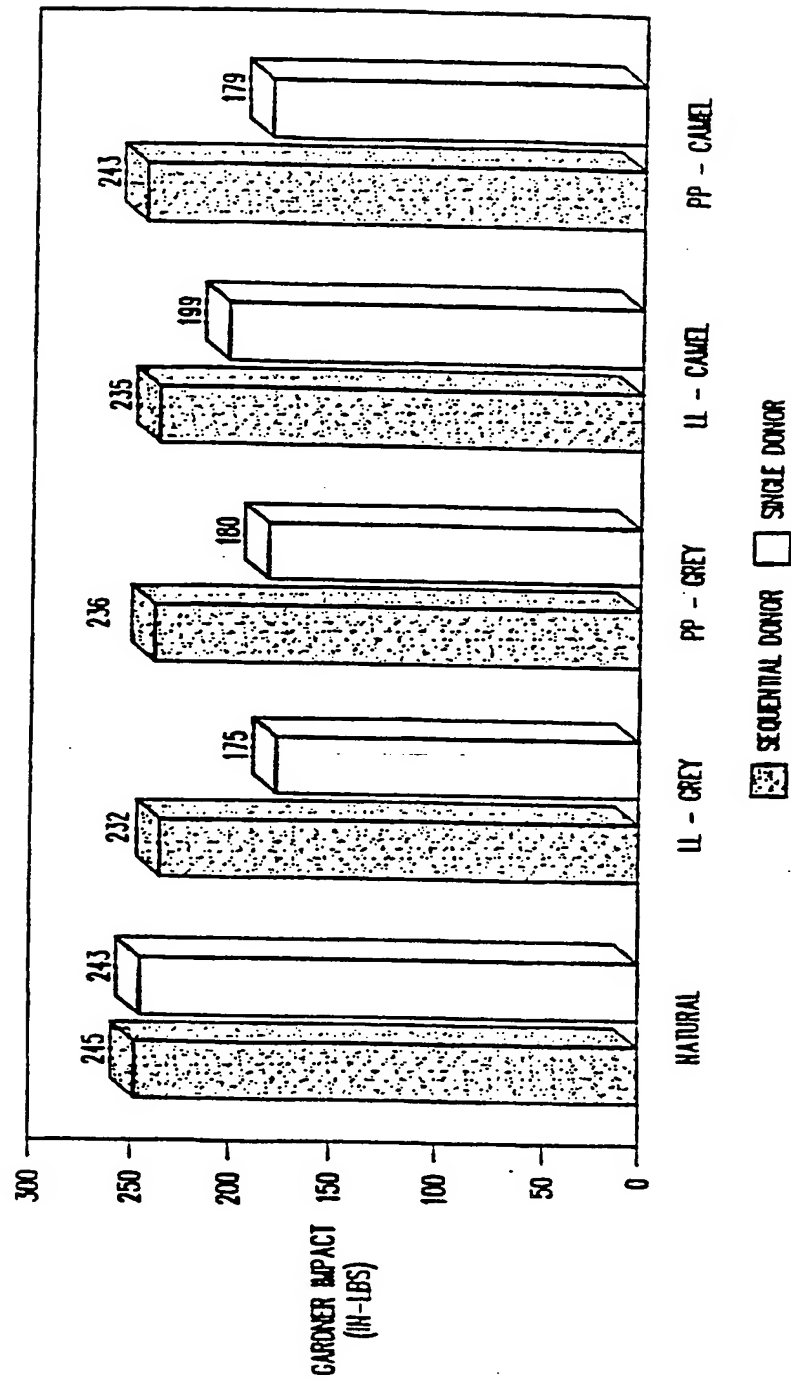
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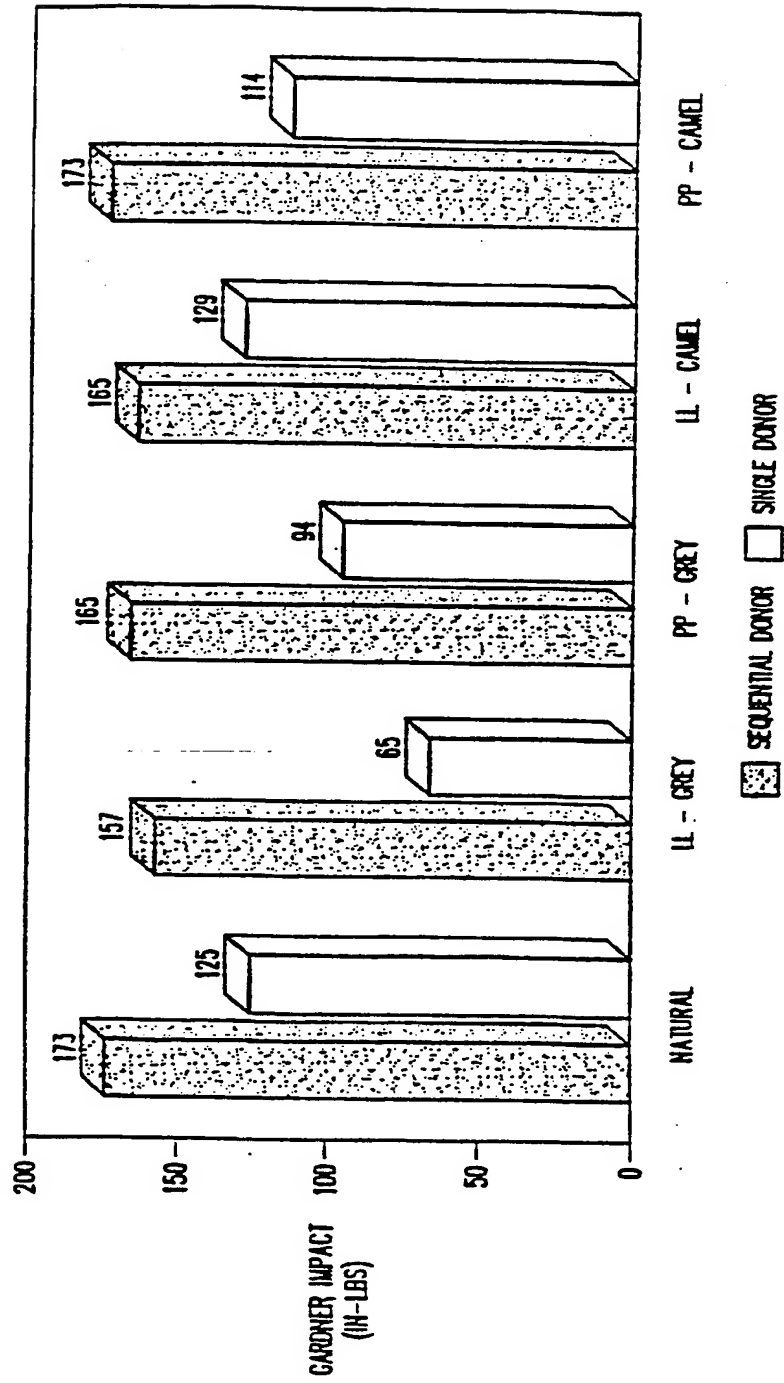


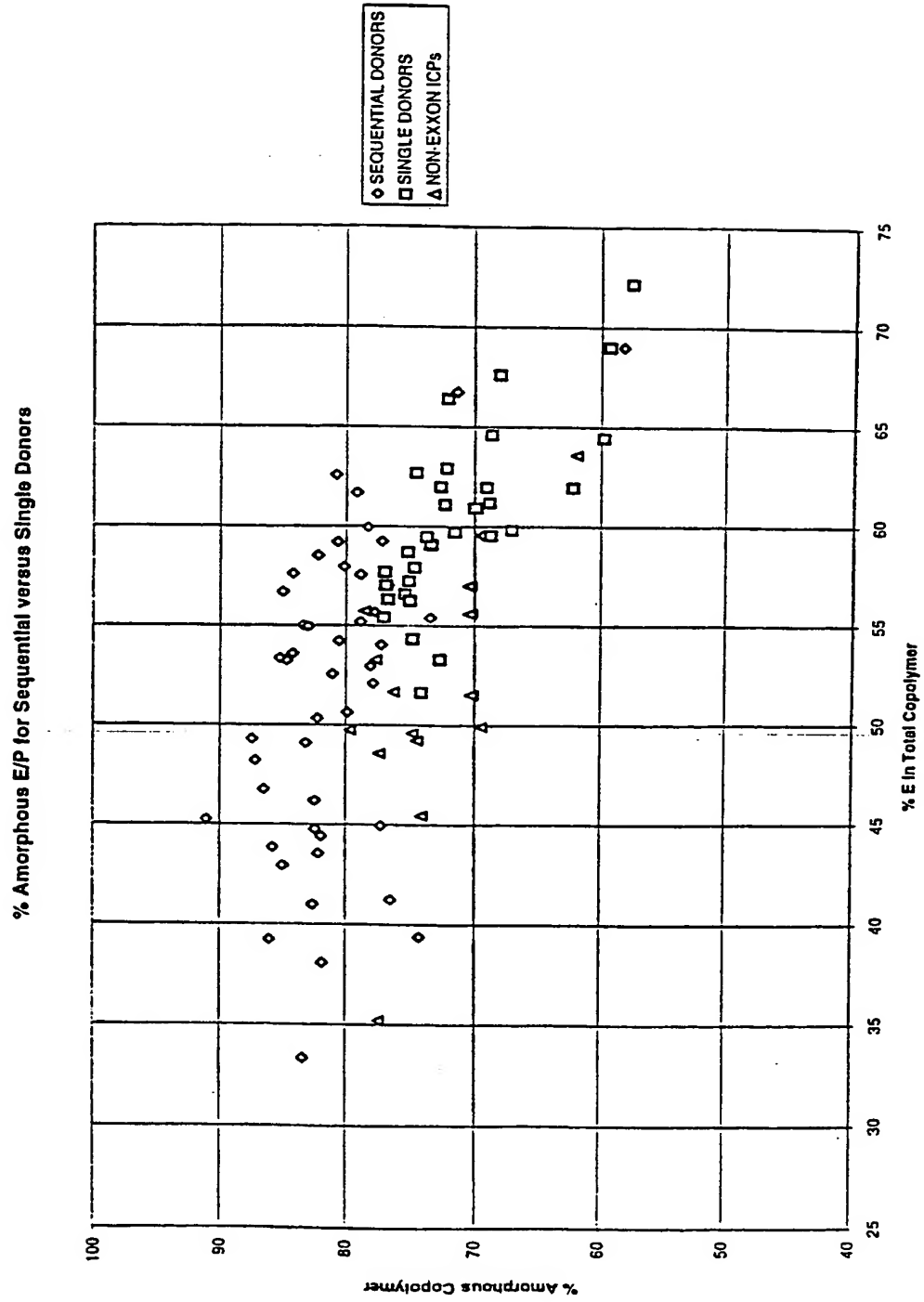
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EFFECT OF NUCEATION - SINGLE vs. SEQUENTIAL DONORS









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(21) International Application Number: PCT/US98/21489 (22) International Filing Date: 13 October 1998 (13.10.98) (30) Priority Data: 08/953,693 17 October 1997 (17.10.97) US (71) Applicant: EXXON CHEMICAL PATENTS INC. [US/US]; 5200 Bayway Drive, Baytown, TX 77520-5200 (US). (72) Inventors: RANDALL, James, C.; 15602 River Maple Lane, Houston, TX 77062 (US). MEKA, Prasadaraao; 2730 Sandpebble Drive, Seabrook, TX 77586 (US). MIRO, Nemesio, D.; 2601 Pine Brook Lane, Seabrook, TX 77586 (US). (74) Agents: SCHMIDT, C., Paige et al.; Exxon Chemical Com- pany, P.O. Box 2149, Baytown, TX 77522-2149 (US).			(81) Designated States: CA, JP, KR, MX, SG, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims</i> <i>and to be republished in the event of the receipt of amendments.</i> (88) Date of publication of the international search report: 2 September 1999 (02.09.99)
(54) Title: HIGH IMPACT, FLEXURAL MODULI POLYMERIC MATERIALS FORMED USING SEQUENTIAL DONORS			
(57) Abstract A method of forming high impact copolymer having a high degree of crystallinity and a melt flow rate of at least 10 to 150. The method preferably comprising: subjecting the α -olefin monomer to an initial polymerization, in the presence of a first electron donor material and a first catalyst to form a polymer product; subjecting the polymer product to a subsequent polymerization, in the presence of a second electron donor material and a second catalyst, thereby forming the α -olefin homopolymer; wherein the second donor material is more stereoregulating than the first electron donor material and the second electron donor material dominates the first electron donor material; and polymerizing a copolymer in the presence of the α -olefin homopolymer; thereby forming a high impact copolymer. The first and second catalysts may be the same or different. The copolymer portion of the high impact copolymer will have an unexpected high amorphous phase content.			

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INTERNATIONAL SEARCH REPORT

International Application No

PC., US 98/21489

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 C08F297/08 C08L23/12 C08L23/16 C08L53/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 95 21203 A (EXXON CHEMICAL PATENTS INC) 10 August 1995 see page 3, line 21 - page 5, line 14 see page 7, line 17 - page 10, line 8 see page 11, line 18 - page 12, line 19 see page 21, line 10 - page 22, line 11; claims; examples ---	1,2,4
Y	GB 2 035 343 A (MITSUBISHI PETROCHEMICAL CO) 18 June 1980 see the whole document ---	1,2,4
X	US 4 493 923 A (J. DOUGLAS MCCULLOUGH, JR.) 15 January 1985 see claim 1 --- -/--	5,8,9

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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G document member of the same patent family

Date of the actual completion of the international search

25 June 1999

Date of mailing of the international search report

07. 07. 1999

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INTERNATIONAL SEARCH REPORT

International Application No

P./US 98/21489

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 552 482 A (BERTA DOMINIC A) 3 September 1996 see column 4, line 44 - line 51; claim 1 ---	5-7
X	EP 0 490 353 A (UNION CARBIDE CHEM PLASTIC) 17 June 1992 see claim 1 ---	9-12
X	US 5 338 801 A (EPPERT JR STANLEY E) 16 August 1994 see claims 1-3 ---	9-12
X	US 5 455 303 A (PANAGOPOULOS JR GEORGE ET AL) 3 October 1995 see claims -----	5-8

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 98/21489

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☒ Claims Nos.: 3
because they relate to subject matter not required to be searched by this Authority, namely:
The electron donor, which forms part of the catalyst system, has to be different in the first and the second reaction step as an essential feature
2. ☒ Claims Nos.: 3
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
The electron donor, which forms part of the catalyst system, has to be different in the first and the second reaction step as an essential feature.
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☒ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-4

Subject-matter of claims 1 - 4 is a polymerization process, which is carried out in three steps. In steps one and two, a homo-alpha-olefin polymer having blocks of different degrees of stereoregularity, caused by the use of different electron donors, is formed and in step three, a copolymer is formed in the presence of the previously prepared homopolymer.

2. Claims: 5-12

Subject-matter of claim 5 - 12 is a high impact copolymer, which comprises a binary copolymer having a high content of amorphous phase and an overall

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/21489

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9521203 A	10-08-1995	AT 166074 T CA 2182717 A CN 1156999 A DE 69502480 D DE 69502480 T EP 0743960 A ES 2119401 T FI 963081 A JP 9508657 T NO 963236 A	15-05-1998 10-08-1995 13-08-1997 18-06-1998 10-12-1998 27-11-1996 01-10-1998 03-10-1996 02-09-1997 25-09-1996
GB 2035343 A	18-06-1980	JP 1434671 C JP 55071712 A JP 61052846 B DE 2946984 A NL 7908507 A,C US 4291138 A	07-04-1988 30-05-1980 14-11-1986 04-06-1980 28-05-1980 22-09-1981
US 4493923 A	15-01-1985	NONE	
US 5552482 A	03-09-1996	EP 0767209 A JP 9118795 A	09-04-1997 06-05-1997
EP 0490353 A	17-06-1992	US 5173536 A AT 123298 T CA 2057471 A DE 69110115 D DE 69110115 T ES 2073104 T JP 2537723 B JP 4323237 A KR 134767 B	22-12-1992 15-06-1995 12-06-1992 06-07-1995 19-10-1995 01-08-1995 25-09-1996 12-11-1992 20-04-1998
US 5338801 A	16-08-1994	AT 158329 T AU 675874 B AU 7583394 A BR 9404160 A CA 2117859 A CN 1106033 A DE 69405676 D DE 69405676 T DK 649872 T EP 0649872 A JP 7157607 A	15-10-1997 20-02-1997 11-05-1995 20-06-1995 21-04-1995 02-08-1995 23-10-1997 26-02-1998 02-02-1998 26-04-1995 20-06-1995
US 5455303 A	03-10-1995	AT 172221 T AU 689876 B AU 2178695 A BR 9502862 A CA 2152157 A CN 1118361 A DE 69505311 D DE 69505311 T EP 0688820 A ES 2125520 T FI 953046 A JP 8003385 A NO 952446 A	15-10-1998 09-04-1998 04-01-1996 30-04-1996 21-12-1995 13-03-1996 19-11-1998 08-04-1999 27-12-1995 01-03-1999 21-12-1995 09-01-1996 21-12-1995